

A LITERATURE REVIEW OF NANOPARTICLE ADDITION TO CONCRETE FOR
NUCLEAR APPLICATIONS

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Dissertation

Submitted to the Faculty of the
Graduate School of Vanderbilt University
in partial fulfillment of the requirements

for the degree of

DOCTOR OF PHILOSOPHY

in

Interdisciplinary Studies

May 11, 2018

Nashville, Tennessee

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*To the members of the family I was born into,
and to my friends, the family I chose,
who have always so kindly supported me*

ACKNOWLEDGEMENTS

I would like to thank my committee chair, Prof. Richard Hoover, for his exceptional leadership and ethics. I would also like to thank my committee members, Prof. Kenneth Debelak, Prof. Frank Parker, and Prof. John Roth, for their commitments of time and insights.

My most profound thanks to the interns whose work supported this dissertation: Marne Helbing, Kate Thomson, Myles Lacy, Ryan Kosson, Matthew Regala, and Aditya Srivastava.

I am very thankful for the many people with whom I have worked along the way: Rossane Delapp, Dave Delapp, Rich Teising, Prof. Mark Wallace, Dr. Kevin Brown, Dr. Lesa Brown, Dr. Jingjing Bu, Dr. Janelle Branch-Lewis, Dr. Timothy Ault, Prof. Joe Biernacki, Baig Al-Muhit, Prof. Douglas Adams, Leslie Gillespie-Marthaler, Dr. Leah Gregor Dundon, Dr. Chelsea Peters, Christopher Tasich, Dr. Erin Decarlo, Darlene Weaver, Beverly Piatt, Karen Fuller, DeeLa McGill, Dalesha Blackwell, Prof. Janet MacDonald, Evan Robinson, and all the kind folks at Graduate Workers United. I would particularly like to thank our collaborators at Oak Ridge National Laboratory: Andres Marquez Rossy, Dr. Edgar Lara-Curzio, Dr. Jorge Navarro, Dr. Geoffrey Deichert, Kory Linton, Dr. Kurt Terrani, and Aaron Selby. I would like to thank Prof. Shihong Lin for allowing our team use of his instruments.

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Finally, I am very thankful for the invaluable support of my parents, Lea and Prof. Ze'ev Reches, my brother Daniel, and my sisters Inbal, Netta, Idit, and Karni.

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NOMENCLATURE

Abbreviation	Description
$\eta_1, \eta_2, \eta_3, \eta_4$	Material- and location-dependent stoichiometric coefficients
CEQM	Concrete-equivalent mortar
CH	Calcium hydroxide
C-S-H	Calcium silicate hydrate
DLS	Dynamic light scattering
EDS	Energy-dispersive X-ray spectrometry
FA	Fly ash
GGBFS	Ground granulated blast furnace slag
GPa	Gigapascal
GWC	Ground waste ceramic
ICP-OES	Inductively-coupled plasma optical emissions spectrometry
ITZ	Interfacial transition zone
MPa	Megapascal
M-S-H	Magnesium silicate hydrate
NP	Nanoparticle
OPC	Ordinary portland cement
RHA	Rice husk ash
SE	Surface energy
SEM	Scanning electron microscope
SF	Silica fume
SSA	Specific surface area
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1. Overview

The present research focused on using nanoparticles (NPs) to enhance the performance of concrete in the nuclear sector, and particularly the storage of spent nuclear fuel. When nuclear fuel rods become depleted, the primary storage solution in the United States is steel-lined pools, where the rods decay for a number of years, then are transferred to concrete dry casks for intermediate-term storage [1] on the order of decades [2]. Over the timescales of years or decades, concrete dry casks may be corroded by a number of conditions, notably outward mass transfer of important constituents (i.e., leaching), inward mass transfer of deleterious constituents (e.g., sulfate attack), elevated temperatures, and gamma radiation [2]. Premature cracking has been observed in some concrete dry casks, and there has been an effort to understand the underlying causes [3].

The approach that was examined in this dissertation for enhancing the durability of concrete to the deleterious effects of mass transfer, elevated temperatures, and gamma radiation was the addition of NPs during mixing. Previously, the incorporation of NPs into portland cement products, including nano-SiO₂, nano-Al₂O₃, nano-Fe₂O₃, nano-TiO₂, nano-CaCO₃, and nano-clays, has been observed to enhance bulk mechanical properties [4], reduce porosity and diffusivity [5-11], and improve durability against extreme exposure conditions such as sulfate attack [12], calcium leaching [13-15], and elevated temperatures [5, 16-18]. It has been suggested that these NPs contribute to the formation of hydrate phases which function to bind cement products, most notably calcium silicate hydrate (C-S-H), by seeding the precipitation of

ions out of solution [19-25], and by reacting with lime of hydration as pozzolana [7, 12, 14, 15, 26-31].

The present review examines the use of NPs as additives to modify concrete used for dry cask nuclear storage.

1.2. Hypothesis

NPs improve the mechanical and durability performance of cement-based materials in conditions of dry cask storage, due to their unique reactivity, which is related to their large specific surface area.

1.3. Literature review

1.3.1. Concrete dry casks for storage of spent nuclear fuel

The present review focused on the application of concrete in the nuclear sector, and particularly the storage of spent nuclear fuel in dry casks (shown in Figure 1.1, and also known as Independent Spent Fuel Storage Installations). These above-ground storage chambers receive an initial license for 20 years of storage, although it has been suggested that their use may, in fact, be extended to 100 years or longer, until a permanent repository becomes available [2]. Premature cracking has been observed in concrete dry casks (Figure 1.2), and there has been an effort to understand the underlying causes [3].



Figure 1.1. Concrete dry casks oriented horizontally (left) or vertically (right) [32]

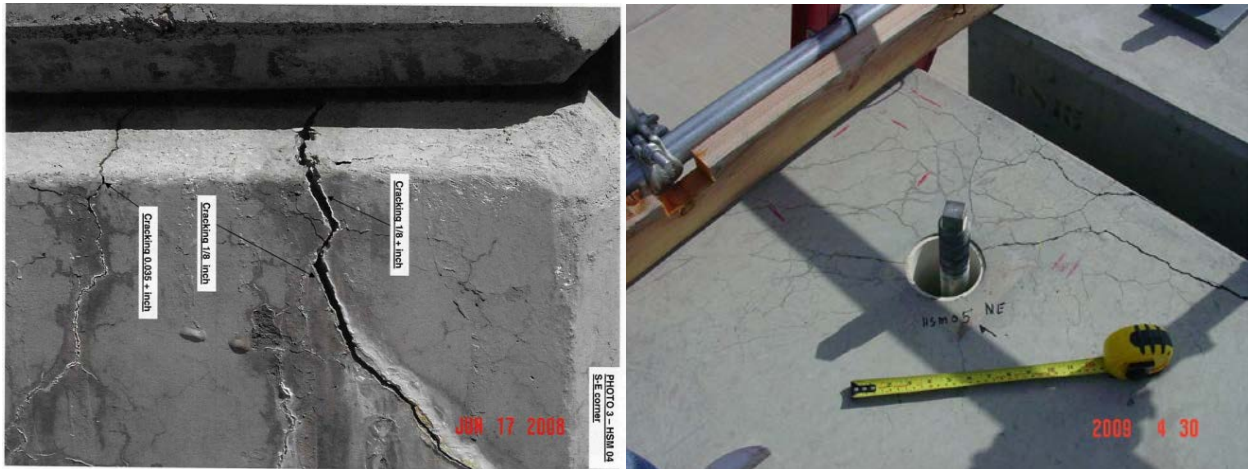


Figure 1.2. Observed cracking of concrete dry cask at Three Mile Island [33]

It has long been reported that radiation may cause a deterioration of the properties of concrete, due to the breakdown of atomic bonds, resulting in cross-linking and embrittlement [34]; radiolysis and thermal dehydration of bound water in cementitious phases, leading to a minor decrease in strength [34, 35]; and an activation of siliceous aggregates, when these aggregates are used, causing the expansive alkali-silica reaction [36]. Exposure to elevated temperatures may also contribute to the degradation of concrete used for dry cask storage, as casks are radiogenically heated by the gamma radiation [37]. Studies to date have focused on conditions relevant for nuclear reactors and pool storage, so that neutron radiation has primarily been used to irradiate specimens of cement-based materials [38, 39]. However, in dry casks, the dominant form of radiation is gamma [40].

1.3.2. Aging and degradation mechanisms of concrete dry casks

During the serviceable lifespan of dry casks, these concrete structures may be corroded by a number of conditions, most notably exposure to environmental weathering, elevated temperatures and gamma radiation [41]. The phenomenon of sulfate attack has been regarded as a particularly important degradation mechanism for concrete dry casks, due to the potential exposure to K_2SO_4 , Na_2SO_4 , $CaSO_4$, and $MgSO_4$ from rainwater and groundwater over the long

lifetime of the casks [42]. Dry casks may be uniquely sensitive to sulfate attack, because the radiogenic heat may cause evaporation of water, and therefore lead to an increased concentration of initially-dilute solutions [37]. The effects of weathering conditions, elevated temperature, and gamma radiation on material properties are discussed below.

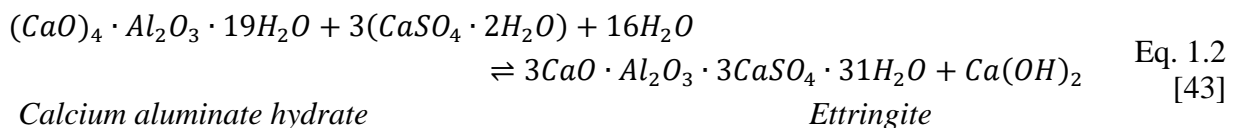
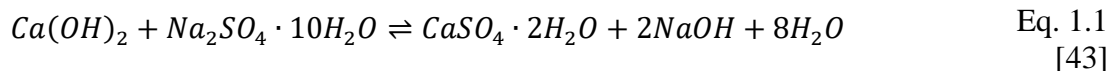
1.3.2.1. Environmental weathering of cement systems

At early ages (hours to months after casting), the chemical, microstructural, and bulk mechanical properties of cement products are governed by the hydration processes of ordinary portland cement (OPC) and any admixtures [43]. Within an element consisting of concrete or mortar, a percolating pore network is formed between the solid structures of clinker phases, hydrates, and aggregates [44]. This network may be partially or fully saturated with a solution (hereafter “porewater solution”), which contains a high concentration of Ca^{2+} , K^+ , Na^+ , OH^- , and SO_4^{2-} dissolved from the OPC and admixtures [45]. Due to the dissolution of KOH, NaOH, and $\text{Ca}(\text{OH})_2$, the pH of the porewater solution is approximately 13 [45]. As the concrete element ages, its internal chemistry gradually equilibrates by continued hydration, which is marked by an increase in pH, a decrease in the concentration of SO_4 in porewater, and the formation of hydrates at the expense of clinker phases [45]. Additionally, the element also equilibrates gradually with its environment through processes which depend on the exposure conditions [46]. As the concentration of certain ions may be higher or lower in the element than in the environment, gradients may form over the cross-section. The transfer of constituents into or out of the cement product proceeds primarily through the pore network [47]. On the bulk scale, the tendency of a porous material such as a cement product to conduct mass transfer by diffusion has been defined as its *observed diffusivity* (also known as the *apparent diffusivity*) [48]. Since mass transfer pathways generally follow large pores, the reduction of total porosity, of pore size, and

of pore connectivity has been a common approach for reducing the observed diffusivity, and therefore enhancing the durability of cement based products to environmental weathering [6, 8-11].

An important weathering mechanism is leaching, whereby the concentration (notably of Ca and/or Si) is higher in the element than in the environment, and the gradient favors outward diffusion of constituents into the environment [46, 49]. Species such as $\text{Ca}(\text{OH})_2$ and C-S-H have been reported to be dissolved into the cement porewater, and diffuse into the surrounding environment (e.g., from precipitation, groundwater, or surface water) through the pore network [14, 49]. This process increases the porosity of the bulk material, and reduces the Ca/Si ratio of the C-S-H phase, ultimately leading to embrittlement and a loss of strength of the cement product [14].

Another key weathering mechanism has been sulfate attack, whereby concentration gradients favor the inward diffusion of sulfate from the environment [46, 50]. Sulfate salts (K_2SO_4 , Na_2SO_4 , CaSO_4 , MgSO_4 , and their respective hydrated forms) from precipitation [42], groundwater [42], or seawater [51] have been reported to react with clinker and hydrate phases, with the most notable reactions expressed nominally as Eq. 1.1 and Eq. 1.2. Per Eq. 1.1, it has been observed that Na_2SO_4 (similarly K_2SO_4) has reacted with calcium hydroxide (CH) formed during hydration of OPC, to form gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Per Eq. 1.2, the gypsum formed in this reaction (or any CaSO_4 which may be present in the environment) has been observed to further react with Al-containing phases [nominally shown as $(\text{CaO})_4\text{Al}_2\text{O}_3 \cdot 19\text{H}_2\text{O}$] to form ettringite.



During the progression of sulfate attack, when the pores of cement products have been water-saturated, sulfate attack has been observed to proceed through inward diffusion of the sulfate salt from the environment, with a parallel outward diffusion of certain soluble species (e.g., K^+ , Na^+ , OH^-) from the cement product [46]. This has been a mass transfer phenomenon, rate-controlled by the *observed diffusivity* of the cement product [46]. In cases where moisture gradients have been present within the cement product (e.g., intermittent wetting/drying, or spatial variation in environmental moisture), advection (i.e., moisture transfer) has been considered as an additional mechanism for the ingress of sulfate ions into the product [46]. The rate of moisture transfer has been quantified using the *permeability* of the cement product [52].

The physical structure of the cement paste phase has been reported to change due to sulfate attack. The primary change that has been reported was related to the expansive nature of the formation of gypsum (Eq. 1.1) and ettringite or similar phases (Eq. 1.2) [43]. An additional mechanism has been the precipitation of sulfate salts in pores due to saturation (e.g., in case of the evaporation of porewater), a mechanism which has also been reported for non-sulfate salts [51]. As a result of either or both of the above mechanisms for the deposition of sulfate minerals in the pore space of the cement products, micro-scale pore-filling, and macro-scale expansion have been observed [53-55]. After the pores of the cement product have been essentially filled with sulfate minerals, micro-scale cracking in the matrix has been observed, resulting in strength loss [51], reduction of modulus of elasticity [56, 57], macro-scale cracking [56], and loss of soundness (i.e., disintegration) [51]. It has been reported that micro-cracks have increased the observed diffusivity of the cement paste phase, causing an acceleration of the ingress of sulfates [57].

Additional physical mechanisms have been observed in the case of MgSO_4 , particularly the formation of a protective layer of $\text{Mg}(\text{OH})_2$ formed during attack of $\text{Ca}(\text{OH})_2$, which has been reported to retard the progression of sulfate attack [51]. The substitution of Mg for Ca during MgSO_4 attack has been reported to weaken cement products, since $\text{Mg}(\text{OH})_2$ and M-S-H have been observed to be mechanically weaker than $\text{Ca}(\text{OH})_2$ and C-S-H, respectively [58].

In field applications, there have been two primary approaches to reducing the effect of sulfate attack on cement-based elements (formulating so-called “sulfate-resistant concrete” [51]):

1. Utilizing OPC and/or admixtures which were less chemically sensitive to sulfate attack [51]. The sensitivity of OPC and admixtures to sulfate attack has been reported to increase with increasing Al_2O_3 content [46], because Al_2O_3 has been observed to contribute to ettringite formation (Eq. 1.2). In OPC considered as moderately sulfate-resistant (i.e., Type II) or highly sulfate resistant (i.e., Type V), the content of tricalcium aluminate (in oxide notation C_3A) has been limited to 8% and 5% by mass, respectively [59].
2. Decreasing the permeability and/or diffusivity of concrete to sulfate-containing solutions [53]. This decrease has most commonly been achieved by the use of a lower water/binder ratio [46], or the use of secondary cementitious materials, particularly ground granulated blast furnace slag (GGBFS), which have decreased the total porosity, pore size, and/or pore connectivity [12, 54, 60-64]. It should be noted that, in some cases, reducing the size and total content of pores has been suggested to increase the severity of sulfate attack, as less pore space was available to accommodate expansion due to precipitation of sulfate minerals

[54], and over the course of years may have the potential to damage dry casks to an important extent.

It is apparent from the above discussion of leaching and sulfate attack that the observed diffusivity of cement products is an important parameter in characterizing their durability to weathering, such as by leaching and sulfate attack. For a well-designed concrete barrier for nuclear waste, typical values for the diffusion coefficient range on the order of 10^{-13} - 10^{-11} m²/s [65].

1.3.2.2. Effects of elevated temperatures on cement products

When concrete is exposed to elevated temperatures, water found in the pores and bound in the cement hydrates is lost [66]. The dehydration of ettringite is completed by 120°C, the dehydration of C-S-H proceeds approximately over the range 120-800°C, and the dehydration of Ca(OH)₂ proceeds approximately over the range of 400-530°C [66]. Beginning circa 100°C, the competing dehydration shrinkage of the cement paste phase and thermal expansion of the aggregates cause microstructural damage, leading to a decrease of strength and modulus of elasticity [67]. The process of damage due to elevated temperatures is rapid, and in the case of fire occurs over the course of hours [5, 18, 68, 71, 73]. In dry casks, this deleterious mechanism may contribute to the degradation of concrete, as casks are heated by the gamma radiation over the course of years or decades [37].

The dehydration of Ca(OH)₂, found as micro-crystals within the cement matrix, to CaO, has reportedly been followed by its expansive rehydration upon cooling [68]. Both the dehydration of hydrates and the subsequent rehydration expansion of CaO may deteriorate mechanical properties [69-71], leading to micro- and eventually macro-scale cracking and spalling [67, 68, 72].

The existing literature on thermal durability of concrete has focused on the context of fire safety. Therefore, it has been common to expose specimens to temperatures on the range of 150-1200°C [5, 18, 68-71, 73]. In dry casks, temperatures may approach 200°C [37].

Most commonly, the durability of cement products to elevated temperatures has been quantified by the firing of specimens, followed by characterization of their mechanical properties (e.g., compressive strength) [5, 18, 69-71, 74], which has yielded an indication of the residual structural integrity of the bulk material following heating.

1.3.2.3. Effects of gamma radiation on cement products

Gamma radiation is considered the primary form of deleterious radiation in dry casks, since the spent rods are clad in a neutron-absorbing material (poison) [75], which protects the concrete from neutron radiation. Table 1.1 summarizes key studies on gamma radiation of cement-based materials. Over the lifespan of a dry cask (i.e., roughly 100 years), a dose on the order of 5,000 MRad is expected [40]. Portland cement mortar exposed to gamma irradiation up to 2,000 MRad has been observed to lose up to 30% of its compressive strength [76]. The following are the primary mechanisms that have been suggested for aging of concrete exposed to gamma radiation under dry conditions:

1. Breakdown of atomic bonds due to irradiation energy, leading to cross-linking of the silica chains in the C-S-H and embrittlement of the bulk cement product [34];
2. Radiolysis and thermal dehydration of bound water, leading to a decrease in strength [34, 35]; and,
3. Shifting of atoms in SiO₂ aggregates (when used) due to impact of photons, causing amorphization and activation for the expansive and damaging alkali-silica reaction [36].

To date, the effects of gamma radiation on portland cement products has been studied primarily within the context of performance of nuclear reactors and wet nuclear storage [77-80]. Consequently, studies have tended to include neutrons as the primary form of deleterious radiation (for example [77, 78]), and samples are generally submerged or wet (for example [77, 79, 80]).

Table 1.1. Summary of conditions and observations from key studies of the effects of gamma radiation on cement-based materials.

Study	Summary	Moisture condition	Dose rate (Rad/h)	Cumulative dose (Rad)	Temperature (°C)	Results
McDowall 1972 [81]	Concrete specimens irradiated unloaded, or loaded at 10 MPa, after 1 year of curing.	Mostly sealed	11.4×10^3	6.8×10^7	30	Shrinkage for non-loaded irradiated concrete was 2-3X of non-irradiated reference. Creep for loaded irradiated concrete was 0.7X of reference.
Gray 1972 [35]	Mortar specimens irradiated after 5 months of curing.	Varied (dry vs. wet)	5.0×10^6	4.7×10^{10}	Not monitored	Mortars lost ~1% of mass. Dimensional changes were minute and varied.
Soo and Millian 1989 [76]	Mortar specimens prepared with CEM I ¹ , CEM V ² , or CEM V with SF were gamma-irradiated, beginning at time of casting.	Set 1: Sealed	3.1×10^3	$1.4-2.6 \times 10^7$	10-20	Compressive strength relative to control: CEM I: 0.85-0.86 CEM V: 0.70-0.89 CEM V with SF: 0.75-0.98
		Set 2: Sealed	3.8×10^5	$4.4-20 \times 10^8$	10-20	CEM I: 0.83-1.02 CEM V: 0.95-1.08 CEM V with SF: 0.98-1.07
Ichikawa and Koizumi 2002 [36]	Quartz, amorphous SiO ₂ slides irradiated, exposed to alkali solution, to represent alkali-silica reaction.	Dry	Not reported	Not reported	20	SiO ₂ was activated for the alkali-silica reaction at a total dose of 5×10^{13} Rad (quartz) or 5×10^{12} Rad (amorphous).

¹CEM I – Type I OPC (general purpose).

²CEM V – Type V OPC (high sulfate resistance).

Table 1.1. Summary of conditions and observations from key studies of the effects of gamma radiation on cement-based materials. – Cont.

Study	Summary	Moisture condition	Dose rate (Rad/h)	Cumulative dose (Rad)	Temp. (°C)	Results
Vodak 2005 [80]	Concrete specimens irradiated after 90 days of curing.	Wet	3.0×10^4	6×10^7	Not monitored	Compressive, tensile strengths at maximum exposure were 0.9X, 0.95X of non-exposed reference, respectively. Porosity was 0.3X of reference.
Lowinska-Kluge and Piszora 2008 [82]	Cement pastes prepared with or without SF, FA, or a proprietary additive irradiated after 90 days of curing.	Not reported	3.8- 4.0×10^6	1.41×10^9	20	Based on visual and SEM observations, cement paste appeared deteriorated by radiation. The effect was apparently mitigated by the author's proprietary additive, but not by SF or FA.
Razaei-Ochbelagh et al. 2010 [83]	Cement paste and mortar specimens irradiated from time of casting.	Sealed	0.50	85	Not monitored	Compressive strength of irradiated cement paste, mortar was 1.6X, 1.9X of non-irradiated reference.

1.3.3. Nanoparticles (NPs) as additives to cement-based materials

NPs as additives to concrete and related cement products have recently been the focus of much research because their uniquely high surface area and reactivity may beneficially modify the workability, mechanical, and durability properties of cement-based materials [4]. Table 1.2 summarizes the effects of NPs on cement-based materials. The first documented, deliberate addition of NPs to a cement-based system occurred in 1964 when Stein and Stevels added nano-SiO₂ to pure alite paste—the most chemically- and physically-simplified surrogate for concrete [84]. Nano-SiO₂ was observed to facilitate a faster and more complete hydration, whose primary product is C-S-H. This discovery signaled great potential for using nano-scale additives to modify the properties of cement-based materials, because polymeric networks of C-S-H are the structural “glue” of concrete and other cement products [4]. Similar effects were observed for OPC paste, by Nelson and Young in 1977 [85]. In spite of these promising preliminary results, the use of NPs as additives to cement-based materials did not appreciably develop until circa 2004 [25, 86-88]. In the following years, a variety of NPs—most notably of SiO₂, Al₂O₃, Fe₂O₃, TiO₂ and clays—have been studied as additives to improve the mechanical and durability properties of cement products [4].

In general, the enhanced mechanical and durability properties have been attributed to the ultrafine size of nano-additives (<100 nm), which gives NPs a very high specific surface area (SSA), surface energy (SE), and reactivity compared to other phases in OPC products (Figure 1.3). Specifically, three mechanisms of action have been proposed: (i) NPs have provided a seeding surface for the deposition of hydrates, and therefore facilitated the hydration of OPC and mineral admixtures (i.e., secondary cementitious materials) [19-25], (ii) nano-SiO₂ [12, 14, 15, 26-31] and potentially also nano-clays [7] have been very pozzolanically reactive, and therefore

have produced cementitious phases (most notably C-S-H) at the expense of portlandite, and (iii) NPs have filled gaps between larger particles (e.g., OPC and mineral admixtures), and therefore densified the packing of the material on the nano- to micro-scale [30, 89, 90].

A large degree of variability has been observed in the contribution of NPs to OPC products. For example, the addition of various types of SiO₂ NPs to mortar at a content of 0.25% per mass of cement was observed to change the 90 day compressive strength relative to the control by -7% and +13% [90]. Similarly, the replacement of 10% of the mass of OPC in mortar with SiO₂ NPs has been shown to increase the compressive strength at 28 days by 34% [91] to 160% [92], for similar mix compositions and particle size of SiO₂ NPs. The replacement of 2.5% of the mass of OPC in mortar with SiO₂ NPs (12 nm), Al₂O₃ NPs (13 nm), and Fe₂O₃ NPs (20-60 nm) has been observed to change the 28 day strength by -43%, +6%, and +12%, respectively [93]. This observed variability has not been well-understood.

Table 1.2. Summary of impact of NPs on concrete components, properties, and reactions (sources in text).

	Concrete (with no NPs)	Effect of NP addition
Components	<ul style="list-style-type: none"> • OPC • Water • Fine aggregate (sand) • Coarse aggregate (gravel) • May contain admixtures (chemical, mineral or fiber) and entrained air 	<ul style="list-style-type: none"> • Nano-scale (typically 4-40 nm) particles of SiO₂, Al₂O₃, Fe₂O₃, TiO₂, CaCO₃, clays or other solid phases
Properties of fresh concrete	<ul style="list-style-type: none"> • Workability/flowability (required for successful casting) • Cohesiveness (i.e., tendency to avoid segregation of concrete into components) • Content of entrained air in concrete (may be advantageous or disadvantageous) • Setting times: <ul style="list-style-type: none"> - Initial (i.e., time when concrete can no longer be worked) - Final (i.e., time when concrete has more than zero nominal compressive strength) 	<ul style="list-style-type: none"> • Reduce workability/flowability by adsorption of water • Increase cohesiveness by adsorption of water • May increase or decrease air content • Shorten setting times by reducing flowability and by accelerating early-age hydration
Hydration reactions	<ul style="list-style-type: none"> • Hydration of OPC into C-S-H and other hydrates (Eq. 1.3) • Pozzolanic reaction (i.e., reaction of mineral admixtures with CH from OPC hydration, which produces secondary C-S-H per Eq. 1.4) • Hydrates (primarily C-S-H) form solid networks and bind aggregates into a matrix 	<ul style="list-style-type: none"> • Nucleate the hydration of OPC and the pozzolanic reaction of mineral admixtures (catalytic role of NPs) • May be pozzolanic (intrinsic reactivity of NPs) • May pack between larger particles (e.g., OPC), and reduce defect size
Properties of hardened concrete	<ul style="list-style-type: none"> • Mechanical <ul style="list-style-type: none"> - Compressive strength (i.e., design strength for structural purposes) - Tensile/flexural strength (indicates tendency for cracking) - Modulus of elasticity (determines strain for a given stress) • Durability <ul style="list-style-type: none"> - Durability to weathering: determined primarily by diffusivity to gases/ions (via porosity, pore size distribution, pore connectivity) - Durability to elevated temperatures 	<ul style="list-style-type: none"> • Generally (with notable exceptions) increase mechanical properties, esp. at early ages • Generally reduce diffusivity and enhance durability

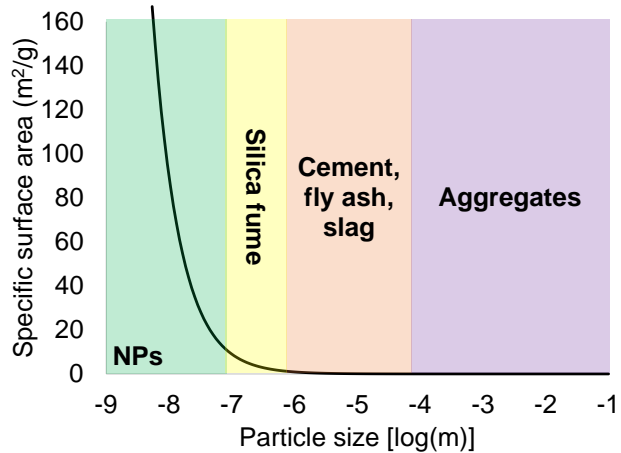


Figure 1.3. Particle size and specific surface area (assuming quasi-spherical geometry and a density of approximately 2.7 g/cm^3) of components in the OPC products. Adapted from [90].

1.3.3.1. Commonly-used NPs

1.3.3.1.1. Size and geometry

While, technically, any particle smaller than 100 nm would qualify as a NP [4], the preponderance of cement research has focused on NPs on the size order of 4-40 nm [5, 8-11, 13, 14, 19, 21-24, 26-31, 86-88, 93-114], with some investigation of NPs on the range of 40-100 nm [6, 18, 93, 106, 109, 111, 112, 115-119]. These sizes represented the size of mono-particles, and the studied NPs have typically been found in agglomerates on the scale of approximately $1 \mu\text{m}$ or larger [21, 22, 27, 117] (the effects of this agglomeration are detailed below).

The majority of examined NPs have been quasi-spherical, that is their aspect ratio was approximately 1. Rods ($10 \text{ nm} \times 40 \text{ nm}$) of nano-rutile- TiO_2 have also been investigated [109], as have nano-clays, shaped as needles or plates (i.e., having one or two dimensions on the nano-scale, and the other(s) on the micro-scale) [6, 7, 116].

1.3.3.1.2. Composition and solid structure

The composition and solid structure of NPs used in a number of key studies are summarized in Table 1.3. The commonly-used compositional types of NPs in cement research

have been nano-SiO₂ [8, 12-14, 17-19, 23-31, 86-88, 91, 93-95, 97-106, 108, 110-114, 116, 120-123], nano-Al₂O₃ [5, 8, 93, 99, 115, 119, 123], nano-Fe₂O₃ [8, 87, 88, 93, 99], nano-TiO₂ [8, 9, 21-24, 107, 109], nano-CaCO₃ [97, 117, 124, 125], and nano-clays [6-8, 97, 116]. A few studies have also examined other NPs, such as nano-MgO [126], nano-CaO [118], nano-Cr₂O₃ [127], nano-CuO [127], nano-ZnO₂ [127] and nano-ZrO₂ [128]. In most cases, NPs have been produced by bottom-up chemical synthesis, such as the sol-gel process [4, 90, 91, 108, 111, 112, 129], though the top-down approach (i.e., milling from bulk phase) has also been used [4, 119].

The solid structure of nano-SiO₂, when reported, has been amorphous [12, 15-17, 19, 25, 27, 29-31, 84, 85, 98, 101, 114, 122]. The solid structure of other NPs has only been reported in a comparatively small number of studies, and included α -Al₂O₃ [123], γ -Al₂O₃ [8, 119], γ -Fe₂O₃ [8], anatase-TiO₂ [8, 10, 21-24, 107], rutile-TiO₂ [109], a composite of anatase- and rutile-TiO₂ [107], bentonite (i.e., montmorillonite) [7, 116], halloysite [6], palygorskite [116] and kaolinite [116].

1.3.3.2. Observed effects of additions of NPs on key properties of hardened ordinary portland cement (OPC) products

1.3.3.2.1. Properties of fresh OPC products

NPs adsorb large quantities of water due to their high SSA [107], causing the fresh concrete mix to become less workable [12, 89, 117, 120] and more cohesive [89, 100]. In general, workability may substantially interfere with successful cast-in-place applications. However, there are niche applications in which these properties would be advantageous (e.g., casting pavement or shotcrete), where increased cohesiveness of nano-modified concrete could help to prevent segregation [129, 130].

NPs have been observed to either increase [120] or decrease [91, 100] the amount of air entrained in concrete. Entrained air produces a combination of advantageous and disadvantageous effects on concrete; most notably, it increases workability, decreases strength, and increases the durability to damage from cycles of freezing and thawing [131].

NPs have been found to accelerate the time required for cement products to set, per Figure 1.4. Typically, it is undesirable to shorten the time to initial set, as this may interfere with important tasks (transportation from the batch plant to the site, inspection, etc.). On the other hand, a shorter final set may be advantageous for rapid construction, because certain tasks (e.g., the use of heavy machinery near recently-cast elements) may not be performed during the time between initial and final set.

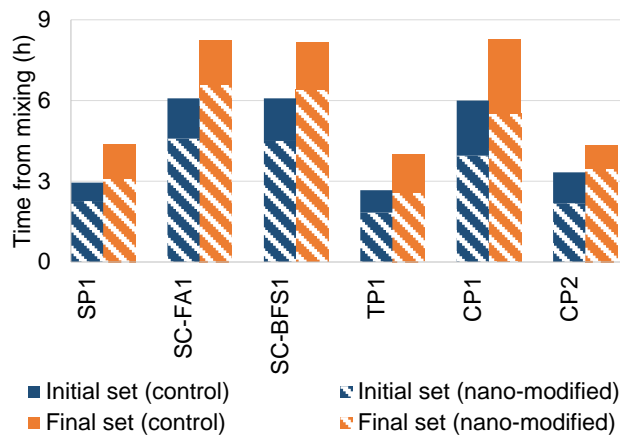


Figure 1.4. Initial and final setting time of cement products made with or without NPs. For key of material names, refer to Table 1.3.

1.3.3.2.2. Mechanical properties of the hardened product

The most prominent design property of concrete is its compressive strength, and this property has commonly been characterized in studies of OPC products with NPs [5-7, 9-11, 13, 15-19, 23, 24, 29-31, 86-88, 90, 91, 93, 94, 96, 97, 99-103, 107-115, 120-125, 132-134]. Tensile strength has also been measured, by flexure or splitting, as an indicator of a material's sensitivity to cracking [10, 13, 17, 18, 24, 29, 87, 88, 105, 111, 120, 125]. In a few cases, the modulus of

elasticity has also been measured, as it governs the material's tendency to strain under stress [5, 109, 110, 120, 123].

Figure 1.5 presents a graphical summary of the properties of 35 different sets of cement-based materials which were modified by the addition of NPs (notably, compressive strength results from [30] were off the charts). As can be readily seen, disparate effects on strength have been observed by different studies. Nevertheless, the following are general trends which have emerged from the literature:

1. The addition of 0.2-10% NPs per mass of binder *generally* increased the compressive and tensile strength of cement products, but in some cases decreased it. At the commonly-used reference point of 28 days, the effect on strength for the cases in Figure 1.5a-c varied from -43% to +53% relative to the control. There was no readily-identifiable dependence on the reported properties of the NPs (composition, particle size, SSA, etc.) or of the cement product (paste vs. mortar vs. concrete, water/binder ratio, use of mineral admixtures, etc.).
2. While numerous studies added NPs at 5-10% of binder mass, the content required to achieve maximum strength was, in most cases, much lower. A peak or plateau in the strength was typically reached at NP contents on the order of 1%, or at the lowest addition which was investigated, with few exceptions.
3. The effect of NPs on strength was typically maximum at ages of 1-7 days. For the cases shown in Figure 1.5d-e, the effect at these early ages ranged from -35% to +81%, relative to the control. The effect diminished as the material matured, and at

ages of more than 28 days, the same studies observed a change in strength on the range from -7% to +24%.

4. The effects of NPs on early-age strength were more pronounced when NPs were added in combination with a slow-reacting mineral admixture, such as fly ash (FA), GGBFS, rice husk ash (RHA), or ground waste ceramic (GWC).

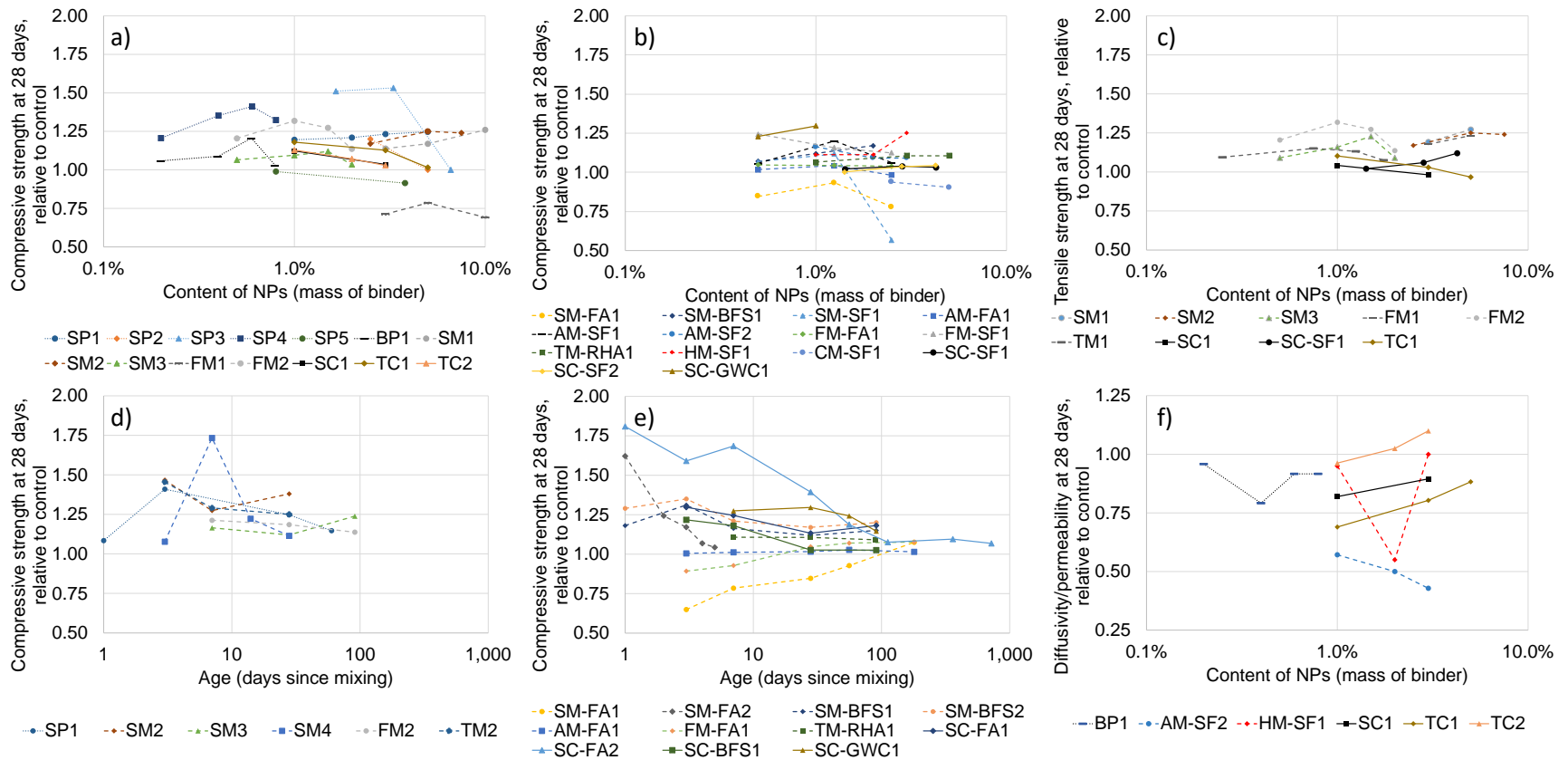


Figure 1.5. Compiled observations from the literature (normalized relative to their respective controls) of cement products containing NPs: a) 28 day compressive strength for OPC products without mineral admixtures, b) 28 day compressive strength for OPC products with mineral admixtures; c) 28 day tensile strength for OPC products with or without mineral admixtures, d) evolution of compressive strength for OPC products without mineral admixtures, e) evolution of compressive strength for OPC products with mineral admixtures, and f) 28 day diffusivity/permeability for OPC products with or without admixtures. For a key of the names for the sample sets, refer to Table 1.3.

Table 1.3. Reported properties for cement products in key studies on the effects of NPs.

NP	Mineral admixture	Name	NP properties				Product composition (per mass binder)			Source	
			Solid structure	Size (nm)	SSA (m ² /g)	Form	NP ¹	Water	Mineral admixture		
Cement paste (i.e., OPC plus NPs and/or mineral admixtures and water)											
SiO ₂	None	SP1	Amorphous	15	160	Powder	0.05	0.22		[29]	
		SP2	Amorphous	10		Colloid	¹	0.40		[19]	
		SP3	Amorphous		390	Colloid	¹	0.45		[85]	
		SP4	Amorphous	20		Colloid	¹	0.55		[31]	
		SP5	Amorphous	10	345	Colloid	¹	0.50		[98]	
TiO ₂	None	TP1	P25 ³	21	59	Powder	0.05	0.35		[107]	
Bentonite	None	BP1	Bentonite	1 ²		Colloid	¹	0.55		[7]	
CaCO ₃	None	CP1		50-120		Powder	0.05	0.32		[117]	
		CP2		15-40	28	Powder	0.03	0.46		[125]	
Mortar (i.e., cement paste plus fine aggregate with size ≤4.75 mm)											
SiO ₂	None	SM1		15	160	Powder	¹	0.50		[88]	
		SM2	Amorphous			Colloid	0.075	0.40		[17]	
		SM3		15	160	Powder	0.015	0.40		[106]	
		SM4	Amorphous	9	300	Colloid	0.1	0.50		[101]	
		FA	SM-FA1		12	200	Powder	0.005	0.40	0.13	[99]
			SM-FA2		12	200	Powder	0.01	0.45	0.49-0.50	[102]
		GGBFS	SM-BFS1		12	200	Powder	0.02	0.45	0.49-0.50	[104]
			SM-BFS2		7	322	Powder	0.01	0.45	0.49-0.50	[104]
Al ₂ O ₃	FA	AM-FA1		13	100	Powder	0.005	0.40	0.13	[99]	
		SF	AM-SF1		13	100	Powder	¹	0.40	0.05	[93]
		AM-SF2		13	100	Powder	¹	0.35	0.05	[5]	

¹This was the NP content in Figure 1.5d-e. In Figure 1.5a-c and f, the NP content varied as shown.

²For clays, the minimum dimension was shown. The length was on the order of μm.

³Commercial name for product of Degussa, which is 75%-25% composite of anatase and rutile, respectively.

Table 1.3 – Cont. Reported properties for cement products in key studies on the effects of NPs.

NP	Mineral admixture	Name	NP properties			Product composition (per mass binder)			Source	
			Solid structure	Size (nm)	SSA (m ² /g)	Form	NP ¹	Water		Mineral admixture
Mortar (i.e., cement paste plus fine aggregate with size ≤4.75 mm)										
Fe ₂ O ₃	None	FM1		30		Powder	¹	0.50		[87]
		FM2		80	560	Powder	0.01	0.40		[106]
	FA	FM-FA1		40	60	Powder	0.005	0.40		[99]
TiO ₂	SF	FM-SF1		40	60	Powder	¹	0.40	0.05	[93]
		None	TM1		15	25	Powder	¹	0.50	
		TM2	Anatase	21	59	Powder	¹	0.35		[107]
	RHA	TM-RHA1		20	200	Colloid	¹	0.40	0.05	[9]
Halloysite	SF	HM-SF1	Halloysite	30-70 ²	64	Powder	¹	0.45	0.05	[6]
CaCO ₃	SF	CM-SF1		15-40		Powder	¹	0.19	0.23	[124]
Concrete (i.e., mortar plus coarse aggregate with size >4.75 mm)										
SiO ₂	None	SC1		10	640	Powder	¹	0.42		[10]
		FA	SC-FA1		12	200	Powder	0.02	0.45	0.48-0.50
		SC-FA2		10	640	Powder	0.04	0.28	0.50	[86]
	GGBFS	SC-BFS1		12	200	Powder	0.02	0.45	0.48-0.50	[102]
	SF	SC-SF1		45	60	Powder	¹	0.25	0.01-0.06	[18]
	GWC	SC-GWC1	Amorphous		200	Powder	0.01	0.50	0.25	[122]
TiO ₂	None	TC1	Anatase	15	240	Powder	¹	0.42		[23]
		TC2		21	50	Powder	¹	0.35		[11]

¹This was the NP content in Figure 1.5d-e. In Figure 1.5a-c and f, the NP content varied as shown.

²For clays, the minimum dimension was shown. The length was on the order of μm.

1.3.3.2.3. Mass transfer properties and durability to weathering

When NPs have been added to cement paste, mortar, or concrete, the observed diffusivity of gases under dry conditions [5-7], and ions under water-saturated conditions [8-11] in the cement products was apparently reduced. Key results are summarized in Figure 1.5. Small NP additions (on the order of 1% by binder mass) reduced the observed diffusivity by a range of 4% to 75% [5-8, 10, 11, 23]. This has been suggested as an important mechanism for the observed efficacy of NPs in improving the structural integrity of cement products exposed to calcium leaching [13-15] or sulfate attack [12].

There has been no readily-identifiable trend regarding the effect of different NPs on the diffusivity of cement products. For instance, He and Shi [8] observed that pozzolanic NPs and NPs with a high SSA were particularly effective at reducing the diffusivity, whereas Zhang and Li [10] observed the opposite trends.

1.3.3.2.4. Durability to elevated temperatures

NPs of SiO₂ [16-18] and Al₂O₃ [5] have generally been observed to increase the resilience of OPC mortars and concretes to elevated temperatures, as measured by their compressive strength before and after thermal exposure (Table 1.4).

Table 1.4. Summary of conditions and observations from key studies of the effects of NPs on the residual compressive strength of mortar and concrete cured 28 days, after exposure to elevated temperatures.

NP	Mineral admixture (per mass binder)	NP properties				Product composition (per mass binder)		Compressive strength relative to control after exposure (°C)					Source
		Solid structure	Size (nm)	SSA (m ² /g)	Form	NP	Water	20	200	400	600	800	
Mortar (i.e., cement paste plus fine aggregate with size ≤4.75 mm)													
SiO ₂	None	Amorphous			Colloidal	0.01-0.05	0.5	1.0-1.2	1.2-1.3	1.1-1.2	1.1-1.2	1.1-1.4	[16]
		Amorphous			Colloidal	0.025-0.075	0.4	1.2-1.4		1.6-1.9			[17]
	FA (0.25)	Amorphous			Colloidal	0.025-0.075	0.4	1.1-1.8		1.0-1.7			[17]
Al ₂ O ₃	SF (0.05)		13	85-115	Powder	0.01-0.03	0.25	1.1-1.2	1.0-1.3	1.0-1.3	0.9-1.1	1.0-1.2	[5]
Concrete (i.e., mortar plus coarse aggregate with size >4.75 mm)													
SiO ₂	FA (0.01-0.11)		45	60	Powder	0.01-0.04	0.35	1.0-1.1		1.0-1.1	1.0-1.2	1.0-1.4	[18]

1.3.3.3. Dispersion/agglomeration state

The dispersion state of NPs has been reported to affect their reactivity, fate and transport [136]. Most notably, as NPs have agglomerated, a fraction of their surface area has become covered, and therefore unavailable for reaction. Accordingly, it has been suggested [5, 90, 100, 108, 133, 134] that care should be taken to properly disperse NPs prior to mixing with OPC, aggregates, admixtures and water. In the majority of cases [5, 6, 9, 11, 13, 15, 21, 22, 26, 29-31, 90, 91, 93, 96, 97, 99, 102-104, 107-109, 111, 112, 114-120, 122, 124, 133, 134, 137], NPs have been added to cement products as nano-powders. Generally [5, 6, 9, 11, 13, 15, 21, 22, 26, 29, 30, 91, 93, 99, 103, 107, 109, 114-118, 122, 124, 133, 134, 137], the nano-powders were simply mixed into the products, whereas in other cases the nano-powders were dispersed in water using ultrasonication, with [96, 97, 120] or without [22, 31, 96, 102, 104, 108, 119, 120, 124] a chemical dispersing agent. In some studies [7, 12-15, 17-19, 27, 28, 31, 98, 100, 101, 108, 115, 121, 133, 137], one or more of the NPs were acquired pre-dispersed (not necessarily mono-dispersed) in an aqueous medium. Unfortunately, chemical and physical dispersion methods used by NP manufacturers have generally been proprietary (e.g., nano-SiO₂ may have been pre-suspended in a saline solution of unknown composition, which may affect cement chemistry).

In some cases [6, 10, 11, 23, 24, 30, 86-88, 98, 105, 121-123, 125], it has been assumed that NPs have been well-dispersed in the cement matrix. In other cases [5, 90, 100, 108, 133, 134], it has been proposed that NPs have agglomerated, and that these agglomerates constituted “weak zones” in the cement matrix. Indeed, sonication of powder-form NPs in water prior to mixing has been observed to enhance the compressive strength [102, 104, 120] and other mechanical properties [120].

Recent work has confirmed that powdered NPs have formed micro-scale agglomerates in hardened cement products [99]. Sonication in water reduced the size of agglomerates by approximately an order of magnitude [138-141]. Dispersing agents such as polycarboxylate-based high-range water reducers have been shown to have some positive effects in terms of facilitating the dispersion of NPs in deionized water [96, 97]. However, even with extensive sonication and the use of a dispersing agent, it was found that a nano-powder of CaCO_3 [96] could not be well-dispersed in water.

1.3.3.4. Proposed mechanisms for the observed effects of NPs on OPC products

1.3.3.4.1. General

The hydration of clinker and mineral admixtures (illustrated in Figure 1.6) is the fundamental process which causes concrete to set and harden. The four primary cementitious phases (in oxide notation these consist nominally of C_3S , C_2S , C_3A , and C_4AF) gradually dissolve, and ions are re-precipitated into hydrates, most notably C-S-H and CH [84]. A nominal representation of this reaction is shown in oxide notation for C_3S in Eq. 1.3. Mineral admixtures with amorphous or slightly soluble SiO_2 (e.g., FA [5, 28, 30], SF [20, 44, 63], GGBFS [48, 50], RHA [55], or GWC [38]) may be added to cement products during formulation, in order to react with CH generated during OPC hydration (Eq. 1.3), and form secondary C-S-H. This process is called the pozzolanic reaction, and nominally proceeds per Eq. 1.4. During the hydration reactions, the volume fraction of hydrates increases at the expense of the fraction of clinker, admixtures, and voids. The interlocking solid network of hydrates (notably C-S-H) functions as the structural backbone of the cement product, and determines its strength, stiffness, and mass transfer properties [1].

$$3C_3S + (3 + \eta_1 - \eta_2)H = C_{\eta_2}SH_{\eta_1} + (3 - \eta_2)CH \quad \text{Eq. 1.3 [43]}$$

$$\eta_3CH + S + \eta_4H = C_{\eta_3}SH_{\eta_3+\eta_4} \quad \text{Eq. 1.4 [43]}$$

where,

$\eta_1, \eta_2, \eta_3, \eta_4$ = material- and location-dependent stoichiometric coefficients.

The hydration process is shown schematically in Figure 1.6a for a control product containing only OPC as binder. The figure shows microstructure of hydration (left columns) from initial stage to late-term, as well as the time evolution of the volume fraction of the various cementitious phases (right column). The hydration of OPC (dark gray) to C-S-H (light gray) and CH (white) causes a reduction in the total content and size of pores (blue). The nanomodification of hydration is shown for non-pozzolanic (TiO_2 , black in Figure 1.6b and e) and pozzolanic (SiO_2 , dark green in Figure 1.6c and f) NPs. The pozzolanic reaction of FA (dark red) into C-S-H and other hydrates (light red) is shown in Figure 1.6d, with the synergistic effect of NPs shown in Figure 1.6e and f.

NPs, whether pozzolanic or non-pozzolanic, serve as nuclei for the precipitation of hydrates from clinker and admixtures (Figure 1.6b, c, e, and f). Pozzolanic NPs generate additional C-S-H (light green) by reaction with CH (Figure 1.6c and f). Below, the main mechanisms of nanomodification are described.

1.3.3.4.2. Seeding of hydration products

It has been proposed [19-24, 114] that NPs facilitate the hydration of clinker *and* the pozzolanic reaction of mineral admixtures, by providing a surface for the deposition of hydrates from the interstitial solution. In order to determine the effects of NPs on early-age hydration (up to approximately 3 days following mixing), isothermal calorimetry has been used to observe the exothermic hydration peak of OPC pastes with and without mineral admixtures. The addition of 0.5-15% nano- SiO_2 [84, 91, 95, 102, 104, 114], nano- Al_2O_3 [119] or nano- TiO_2 [21, 22, 107] accelerated the development of the peak, and increased the total heat of hydration (indicating a

greater extent of reaction over the experimental timeframe). Li [86] observed the effects of seeding even at longer timeframes (weeks to months), based on the mass of C-S-H that was formed per Eq. 1.4.

The catalytic role of NPs in the reaction of other cementitious phases has been considered as important because of the function of C-S-H as the structural backbone of cement products [4]. As C-S-H—and particularly the high-stiffness variety of C-S-H—has formed at the expense of CH and/or pores, the stiffness of the micro-structure was increased, leading to a stronger and stiffer bulk cement product [15, 19, 28]. Additionally, the formation of C-S-H and other hydrates has been suggested to decrease the total porosity [6, 7, 10, 23, 98, 104, 107] (summarized in Figure 1.7), refine the size distribution of pores [10, 31, 86, 91, 95, 103, 104, 107, 109, 132], and reduce the pore connectivity [8-10, 134]. The combination of these mechanisms has been attributed as the primary reason for the observed reductions of material diffusivity [6, 8-11].

NPs have been observed to play a particularly important role in facilitating the pozzolanic reaction of slow-reacting admixtures, based on indirect evidence, such as acceleration of the evolution of strength in cement products containing FA [11, 17, 86, 96, 99, 102, 117, 121], GGBFS [102, 104], RHA [9], and waste sludge ash [103] (Figure 1.5).

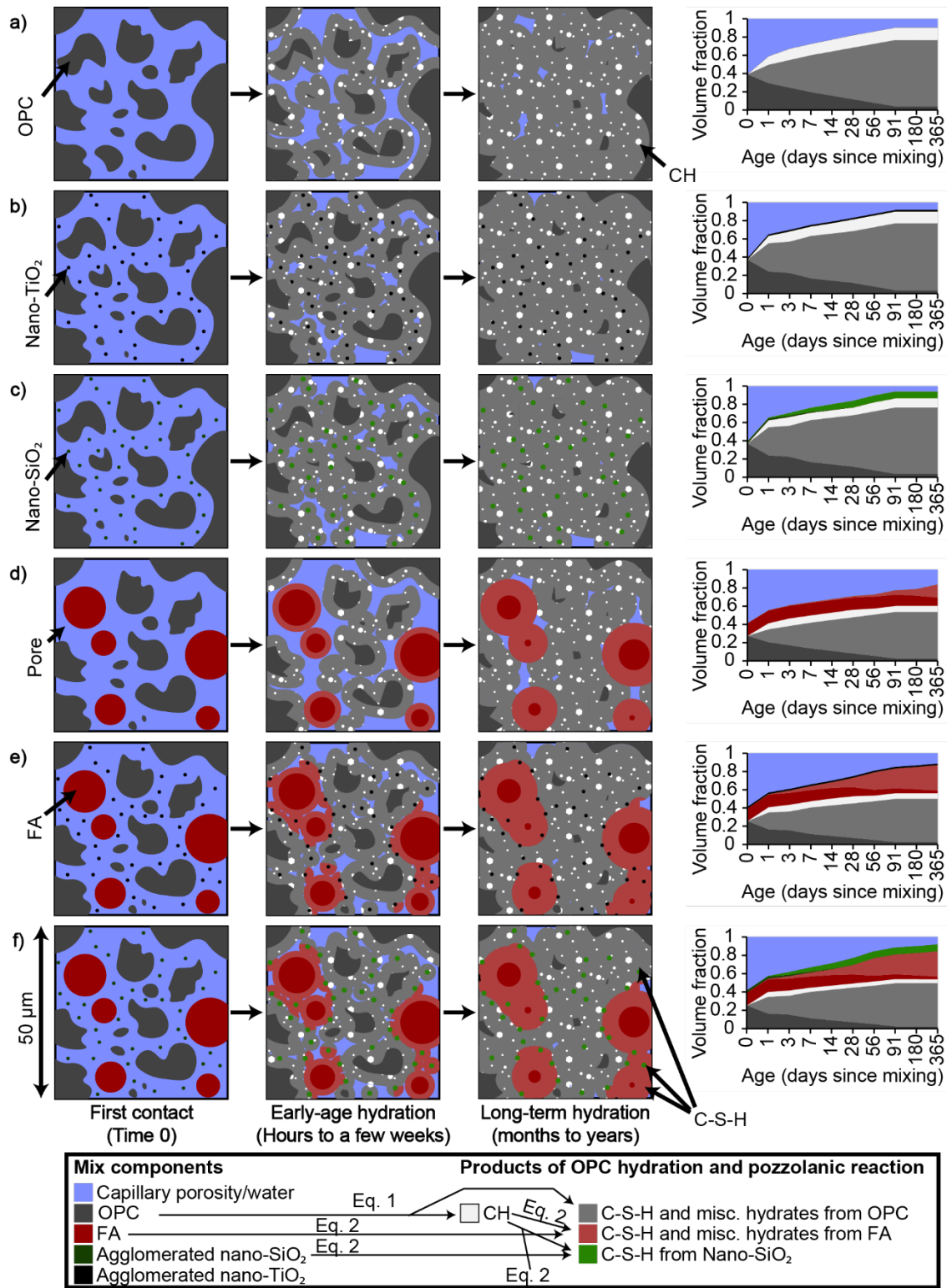


Figure 1.6. Conceptual model (adapted from [22, 119]) for hydration of cement products containing: a) OPC, b) OPC with nano-TiO₂ (non-pozzolanic), c) OPC with nano-SiO₂ (pozzolanic), d) OPC with FA, e) OPC with FA and nano-TiO₂, f) OPC with FA and nano-SiO₂.

Table 1.5. Summary of conditions and observations from key calorimetry studies of NPs in cement pastes.

NP	Mineral admixture (per mass binder)	NP properties				Product composition (per mass binder)		Calorimetric observations		Source
		Solid structure	Size (nm)	SSA (m ² /g)	Form	NP	Water	Peak heat flux (h) of control (nano-modified)	Total heat (J/g) of control (nano-modified)	
SiO ₂	None	Amorphous		207	Powder	0.025	1	5 (4)		[84]
			30-100	Powder	0.05	0.5	5 (4)		[91]	
		Amorphous	4	400	Colloid	0.05	0.4	7 (4)		[95]
		Amorphous	10	200	Colloid	0.05	0.4	7 (5)		[95]
		Amorphous	20	100	Colloid	0.05	0.4	7 (5)		[95]
	FA (0.49-0.50)		12	200	Powder	0.01	0.45	11-15 (10-13)	80 (100)	[102]
	GGBFS (0.49-0.50)		12	200	Powder	0.01	0.45	10-20 (9-18)	115 (120)	[104]
Al ₂ O ₃	None	γ	57	146	Powder	0.005-0.1	0.5	8 (8-11)		[119]
TiO ₂	None	Anatase	20-30	45-55	Powder	0.05-0.1	0.5	8-10 (7-9)	270 (290-300)	[21]
		Anatase	15-25	75-95	Powder	0.05-0.1	0.5	8-10 (5-8)	270 (300-320)	[21]
		Anatase	6	612	Powder	0.05-0.15	0.5	9-11 (8-10)	255 (305-335)	[22]
		P25 ¹	21	59	Powder	0.05-0.1	0.35	10 (7)	225 (250)	[107]
		Anatase	350	8	Powder	0.05-0.1	0.35	10 (9)	225 (250)	[107]

¹Commercial name for product of Degussa, which is 75%-25% composite of anatase and rutile, respectively

Concrete and mortar are composite materials, whose primary phases consist of cement paste and aggregates. The porosity of the interfacial transition zone (ITZ) between these phases has been observed to be higher than the rest of the cement paste, because the aggregate inhibits optimal packing of particles of OPC and mineral admixtures (the so-called “wall effect”) [94]. The increased porosity of the ITZ compared to the bulk cement paste phase has been reported to diminish the mechanical properties [142, 143], and increase the diffusivity of the composite [144]. It has been proposed that NPs, due to their small size, may pack closer than OPC to the aggregate surface, where NPs’ seeding of hydration products has served to densify the ITZ and enhance the mechanical and durability properties of the concrete [94, 100, 123].

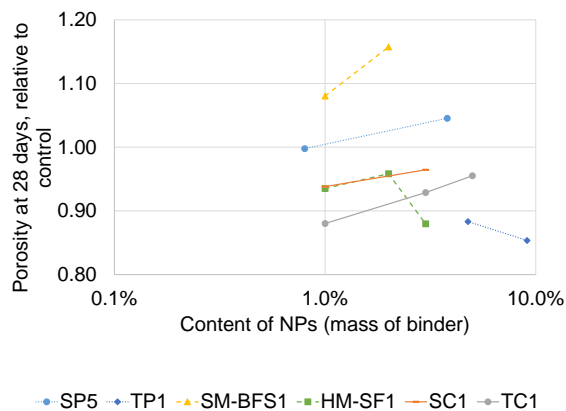


Figure 1.7. Observations from the literature of 28 day porosity of cement products prepared with NPs, normalized relative to their respective controls. For key of names for the sample sets, refer to Table 1.3.

1.3.3.4.3. Pozzolanic reaction

In Section 1.3.3.4.2, the effect of NPs on the hydration of *other phases* was discussed, including the pozzolanic reaction of traditional mineral admixtures, such as GGBFS. In this section, the pozzolanic reaction of *the NPs themselves* (particularly nano-SiO₂ and nano-clays) is considered. Due to its large SSA, nano-SiO₂ has been reported to react pozzolanicly up to 10X faster than silica fume (SF) [95], a micro-scale pozzolanic material containing approximately 90% SiO₂. The *ultimate product* of the pozzolanic reaction was apparently comparable between

SF and two types of colloidal nano-SiO₂ (diameters 4 nm and 20 nm), which all formed C-S-H with a CH:SiO₂ mass ratio of approximately 2:1 (i.e., the molar ratio η_3 , in Eq. 1.4 was approximately 1.6). A third type of nano-SiO₂ (10 nm) was found to react with $\eta_3 \approx 2.4$, indicating that a different C-S-H structure was formed [95]. In fact, it has been proposed [14, 15, 27, 28] that the pozzolanic reaction of nano-SiO₂ has tended to form more “high-stiffness” C-S-H (i.e., having an elastic modulus on the order of 22-31 GPa [28]), as opposed to “low-stiffness” C-S-H (i.e., having an elastic modulus on the order of 11-22 GPa [28]) than is typically generated during the hydration of OPC. High-stiffness C-S-H was suggested as more mechanically and chemically resilient than low-stiffness C-S-H, and it has been hypothesized that its formation may contribute to observed changes in bulk material properties.

1.3.3.4.4. Packing density

NPs are finer by approximately 1-2 orders of magnitude than OPC and traditional mineral admixtures [111] (Figure 1.3). It has been suggested [30, 89, 90], that NPs therefore extend the gradation of cement products, and fill the gaps between other particles. Although NPs are small enough that they *could* fill in gaps between larger particles, it would be difficult to demonstrate that they *actually do*, and that this gap-filling remains relevant following hydration. Furthermore, NPs in the cement system have been found not as individual particles, but as micro-scale agglomerates [21, 22, 27, 117], which would be on the length-scale of other products in the cement system (Figure 1.3), and it has been proposed that agglomeration may prohibit a unique gap filling mechanism of NPs [145].

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